A Cell for Countercurrent Electromigration Experiments for Molten Nitrates

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Dedicated to the 65th Birthday of Professor A. Klemm

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A new type of cell for countercurrent electromigration of molten nitrates is proposed, in which molten NH_4NO_3 is employed just above its melting point in a large cathode compartment. This cell can be used effectively without trouble of corrosion for the purpose of (1) enrichment of ^6Li, (2) enrichment of heavier isotopes such as ^7Li, and (3) measurements of relative internal mobility differences of cations and/or isotopes.

Introduction

Since Klemm et al. invented the method of countercurrent electromigration of molten salts some thirty years ago [1], the method has been employed by many researchers mainly for (1) isotope separations, (2) measurements of elementary separation factors and (3) measurements of relative internal mobility differences of mixtures. While Klemm et al. tried the method in molten chloride systems at first, Hoover and Holloway applied the method also to a molten nitrate system in an attempt to enrich lithium isotopes [2]. By using this technique, Lundén and coworkers have carried out extensive studies to measure isotope effects [3] and relative internal mobility differences [4] in molten pure and mixed nitrate systems. One of the points to be improved in this technique would be the way how to prevent electrodeposition of metals at the cathode without trouble of corrosion. In molten nitrate systems usually a mixture of NO_2 and O_2 was introduced into the cathode compartment. In an alternative way, NH_4NO_3 mixed with other molten nitrates was used in the whole cell [5]. In either way, however, lighter isotopes such as ^6Li could not substantially be enriched at the cathode.

In a previous attempt to enrich ^6Li in molten nitrate systems we proposed a method in which pure NH_4NO_3 was used in the cathode compartment and ^6Li was enriched near the region of transition from NH_4NO_3 for $LiNO_3$, which was placed in a diaphragm part of a separation tube [6]. In the present paper a modified electromigration cell is proposed, which can be used for the purposes mentioned later.

Electromigration Cell

The cell (Fig. 1) is composed of three parts: A large container (A), a large cathode compartment (B 1) connected with a separation tube (B 2), and another separation tube (C). In order for the inside of the cell to be observed from the outside, it is advisable that the cell be made of transparent quartz glass and placed inside furnaces made of transparent glass. Both the top and the bottom of B 2 are installed with quartz filters, and the middle part is packed densely with alumina powder. B is inserted into A. The lower part of the container

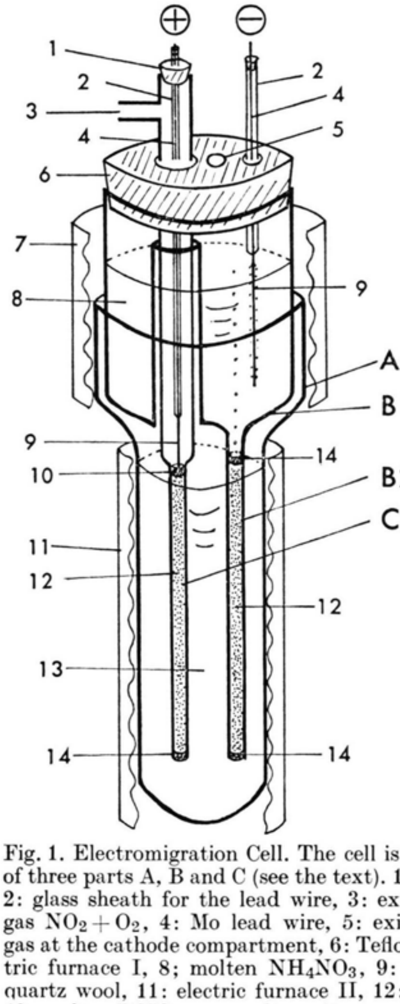

Fig. 1. Electromigration Cell. The cell is composed mainly of three parts A, B and C (see the text). 1: Silicone stopper, 2: glass sheath for the lead wire, 3: exit for the evolved gas $NO_2 + O_2$, 4: Mo lead wire, 5: exit for the evolved gas at the cathode compartment, 6: Teflon stopper, 7: electric furnace I, 8; molten NH_4NO_3, 9: Pt electrode, 10: quartz wool, 11: electric furnace II, 12: alumina powder, 13: molten $LiNO_3$ or a molten nitrate mixture, 14: quartz filter.

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is filled with either molten $LiNO_3$ or a molten nitrate mixture according to the purposes stated later. Then, NH_4NO_3 is filled into B 1, which is heated with the electric furnace I just above the melting point of NH_4NO_3 (169.6 °C). Meanwhile, the lower part of A is heated with the electric furnace II. When the lower part of A is heated at relatively high temperatures, say, above 400 °C, it is not necessary to heat B 1 with the furnace I. In this case B 1 should be kept suitably apart from the level of the molten salt in A by raising it. The separation tube C, fitted at the bottom with quartz filter, is densely filled with alumina powder and covered with a piece of quartz wool. Then it is filled with a molten salt either in another vessel [7] or in A according to the purpose of experiments. Electrolysis is carried out with Pt wires for both cathode and anode.

The composition of the gases evolved at the cathode compartment has not been analyzed; however, ammonia gas is supposed from its smell to be contained in the gas. It is known that the products of the thermal decomposition of NH_4NO_3 just above the melting point are N_2, N_2O and H_2O [8]. The H_2O product does not have any serious effect on the electromigration experiments. In a long run of electromigration, molten NH_4NO_3 must be added to the cathode compartment either at regular intervals (e.g. once a day) or automatically by detecting a decrease of the level. The NO_2 gas evolved at the anode can be treated, if necessary, by introducing it into the cathode compartment, where it will react with the NH_3 gas. To avoid complexity, the thermocouple is not shown in Figure 1. It is inserted into the salt in A along the tube C.

Application

It has been found that in the molten $LiNO_3$-NH_4NO_3 mixtures NH_4^+ migrates faster than Li^+ under all accessible temperatures and concentrations [9]. If B 2 is kept approximately above 220 °C, NH_4NO_3 penetrating into B 2 is thermally decomposed into gases. Therefore, if one uses pure $LiNO_3$ as the salt in the container A, the boundary between $LiNO_3$ and NH_4NO_3 can be kept rather sharp around the top of B 2 irrespective of the duration of the electromigration. Thus, by using $LiNO_3$ everywhere except in B 1, ^6Li can be enriched toward the cathode in B 2, a portion of the enriched material diffusing into B 1, and, meanwhile, ^7Li can be enriched toward the anode in C. If one is interested only in enrichment of ^6Li, C can be removed. On the other hand, if one only wants to enrich ^7Li, B2 can be made shorter in length and larger in diameter. In an experiment ^6Li could be enriched from 7.5% to 90.0% with a length of 25 cm for B 2 in 38 days [10]. In another experiment, ^7Li could be enriched from 92.5% to 99.986% with a diaphragm length of 35 cm in 49 days [11].

The cell can be used also for measurements of relative differences in internal mobilities of two cations in a binary or ternary nitrate mixture. In this case, binary or ternary mixtures such as $LiNO_3$-$NaNO_3$-KNO_3 are recommended as the salt in the container A so that a wide range of temperatures can be covered. The separation tube C should be fillled in a separate vessel with the molten salt of the composition under study and transferred into A just before electromigration [7]. With this procedure, electromigration can be carried out readily at various compositions one after another. It is of course necessary to stop electromigration while the composition remains undisturbed in an extended range around the middle of the diaphragm part. With cells of this type we have so far determined the relative mobility differences of binary systems such as $LiNO_3$-$NaNO_3$, $LiNO_3$-$RbNO_3$ and $LiNO_3$-$CsNO_3$. In a similar way, relative differences in internal mobilities of two isotopic cations, that is elementary separation factors, can be measured, if the diaphragm part is long enough.

This cell is restricted in its application in that it cannot be used for enrichment of the lighter isotope of cations, such as ^{39}K, whose mobility is smaller than that of NH_4^+. Otherwise, this cell can conveniently be used without trouble of corrosion for the purposes stated above.

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